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(54) **Syndiotactic polypropylene.**

(57) The invention provides a new structure for syndiotactic polypropylene in which the microstructure of the polymer chain consists of blocks of repeating racemic (r) dyads being predominantly connected by units consisting of a meso triad (mm). The polymer is also highly crystalline and consists of a high percentage of racemic (r) dyads.

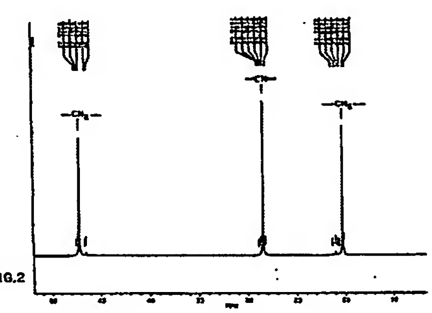


FIG.2

Description

SYNDIOTACTIC POLYPROPYLENE

TECHNICAL FIELD

The invention relates to syndiotactic polypropylene and more particularly to a novel structure for syndiotactic polypropylene.

BACKGROUND OF THE INVENTION

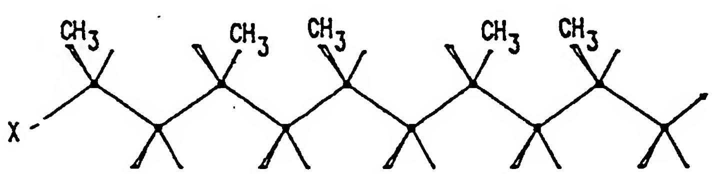
The present invention provides a highly crystalline, novel microstructure of syndiotactic polypropylene.

As known in the art, syndiotactic polymers have a unique stereochemical structure in which monomeric units having enantiomorphic configuration of the asymmetrical carbon atoms follow each other alternately and regularly in the macromolecular main chain. Syndiotactic polypropylene was first disclosed by Natta et al in U.S. Patent No. 3,258,455. The Natta group obtained syndiotactic polypropylene by using a catalyst prepared from titanium trichloride and diethyl aluminum monochloride. A later patent to Natta et al, U.S. Patent No. 3,305,538, discloses the use of vanadium triacetylacetonate or halogenated vanadium compounds in combination with organic aluminum compounds for producing syndiotactic polypropylene. U.S. Patent No. 3,364,190 to Emrick discloses a catalyst system composed of finely divided titanium or vanadium trichloride, aluminum chloride, a trialkyl aluminum and a phosphorus-containing Lewis base as producing syndiotactic polypropylene.

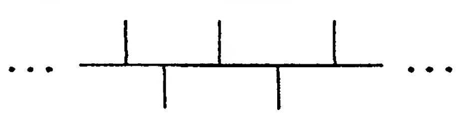
As disclosed in these patent references and as known in the art, the structure and properties of syndiotactic polypropylene differ significantly from those of isotactic polypropylene. The isotactic structure is typically described as having the methyl groups attached to the tertiary carbon atoms of successive monomeric units on the same side of a hypothetical plane through the main chain of the polymer, e.g., the methyl groups are all above or below the plane. Using the Fischer projection formula, the stereochemical sequence of isotactic polypropylene is described as follows:

Another way of describing the structure is through the use of NMR. Bovey's NMR nomenclature for an isotactic pentad is ...mmmm... with each "m" representing a "meso" dyad or successive methyl groups on the same side in the plane. As known in the art, any deviation or inversion in the structure of the chain lowers the degree of isotacticity and crystallinity of the polymer.

In contrast to the isotactic structure, syndiotactic polymers are those in which the methyl groups attached to the tertiary carbon atoms of successive monomeric units in the chain lie on alternate sides of the plane of the polymer. Syndiotactic polypropylene is shown in zig-zag representation as follows:



Using the Fischer projection formula, the structure of a syndiotactic polymer is designated as:



In NMR nomenclature, this pentad is described as ... rrrr... in which each "r" represents a "racemic" dyad, i.e., successive methyl groups on alternate sides of the plane. The percentage of r dyads in the chain determines the degree of syndiotacticity of the polymer. Syndiotactic polymers are crystalline and like the isotactic polymers are insoluble in xylene. This crystallinity distinguishes both syndiotactic and isotactic polymers from atactic polymer that is soluble in xylene. Atactic polymer exhibits no regular order of repeating unit configurations in the polymer chain and forms essentially a waxy product.

While it is possible for a catalyst to produce all three types of polymer, it is desireable to have catalysts that produce predominantly isotactic or syndiotactic polymer with very little atactic formed. Catalysts that produce isotactic polyolefins are disclosed in copending U.S. Patent Application Serial Nos. 034,472 filed April 3, 1987;

096,075 filed September 11, 1987; and 095,755 filed on September 11, 1987. These applications disclose chiral, stereorigid metallocene catalysts that polymerize olefins to form isotactic polymers and are especially useful in the polymerization of a highly isotactic polypropylene. The present invention, however, utilizes a different class of metallocene catalysts that are useful in the polymerization of syndiotactic polyolefins, and more particularly syndiotactic polypropylene.

The present invention provides syndiotactic polypropylene with a new microstructure. It was discovered that the catalyst structure not only affected the formation of a syndiotactic polymer as opposed to an isotactic polymer, but it also appears to affect the type and number of deviations in the chain from the principally repeating units in the polymer. Previously, the catalysts used to produce syndiotactic polypropylene were believed to exercise chain-end control over the polymerization mechanism. These previously known catalysts, such as the ones disclosed by Natta et al in the references cited above produce predominately syndiotactic polymers having the structure

or in NMR nomenclature ...rrrrmrrrr.... The NMR analysis for this structure of syndiotactic polypropylene is shown in Zambelli, et al., Macromolecules, Vol. 13, pp 267-270 (1980). Zambelli's analysis shows the predominance of the single meso dyad over any other deviation in the chain. It was discovered, however, that the catalysts disclosed herein produce a polymer with a different microstructure than that previously known and disclosed, and in addition one having a high percentage of racemic dyads in the structure.

SUMMARY OF THE INVENTION

The present invention provides syndiotactic polypropylene having a high syndiotactic index and with a novel microstructure. Further, the syndiotactic polypropylene has a high crystallinity and may be produced with either a broad or narrow molecular weight distribution. The novel microstructure for the syndiotactic polypropylene of the present invention has blocks of repeating racemic (r) dyads predominantly connected by units consisting of a pair of meso (m) dyads, i.e., a meso triad "mm." The predominant structure of the polymer chain is thus described in NMR nomenclature as ...rrrmmrrr .... In addition, the polymer chain preferably consists of greater than 80% racemic dyads, and most preferably, greater than 95% racemic dyads.

The novel microstructure is obtained through use of a stereorigid metallocene catalyst described by the formula

$R''(CpR_n)(CpR'_m)MeQ_k$

wherein each Cp is a cyclopentadienyl or substituted cyclopentadienyl ring; each R_n and R'_m is a hydrocarbyl radical having 1-20 carbon atoms; R″ is a structural bridge between the two Cp rings imparting stereorigidity to the Cp rings; Me is a transition metal; and each Q is a hydrocarbyl radical or is a halogen. Further, R'_m is selected so that (CpR'_m) is a sterically different substituted cyclopentadienyl ring than (CpR_n). It was discovered that the use of a metallocene catalyst as described above with cyclopentadienyl rings that are sterically different in terms of their substituents, produces syndiotactic polypropylene having the novel microstructure described above.

The novel microstructure of syndiotactic polypropylene is obtained by introducing at least one of the catalysts described by the above formula into a polymerization reaction zone containing propylenemonomer. In addition, an electron donor compound and/or a cocatalyst such as alumoxane may be introduced into the reaction zone. Further, the catalyst may also be pre-polymerized prior to introducing it into the reaction zone and/or prior to the stabilization of reaction conditions in the reactor.

The present invention also includes a process for producing syndiotactic polypropylene having a broad molecular weight distribution. This process comprises utilizing at least two different catalysts described by the above formula in the process of polymerization.

It was further discovered that the characteristics of the polymer produced by the process of polymerization described herein could be controlled by varying the polyermization temperature or the structure of the catalyst. In particular, it was discovered that a higher polymerization temperature resulted in a syndiotactic polymer with more of a mixed microstructure although the meso triad still predominates over the meso dyad in the polymer chain. Also, it was discovered that the melting points of the polymer are affected by the reaction temperature, the catalyst-cocatalyst ratio, and the structure of the catalyst. A higher reaction temperature generally produces a less crystalline polymer having a lower melting point. Further, polymer products with different melting points are obtainable by using a catalyst with a different structure.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is an illustration of the structure of a preferred catalyst useful in producing the novel syndiotactic structure. FIGURE 1 specifically shows iso-propyl(cyclopentadienyl) (fluorenyl) hafnium dichloride.

FIGURE 2 is an NMR spectra for the polymer produced in Example 1 with the polymer being

recrystallized once from xylene.

FIGURES 3 and 4 are IR spectra for the polymers produced in Examples 7 and 8 respectively with the polymer being recrystallized three times from xylene.

DETAILED DESCRIPTION

The present invention provides syndiotactic polypropylene with a novel microstructure. This novel structure consists of blocks of racemic dyads connected predominantly by units consisting of a pair of meso dyad. As described in NMR nomenclature, the structure ...rrrmmrrrr.... The polymer consists of a high percentage of racemic dyads and is highly crystalline. It can be produced to varying specifications for melting points, molecular weights, and molecular weight distributions.

When propylene or other alpha-olefins are polymerized using a catalyst consisting of a transition metal compound, the polymer product typically comprises a mixture of amorphous atactic and crystalline xylene insoluble fractions. The crystalline fraction may contain either isotactic or syndiotactic polymer, or a mixture of both. Highly iso-specific metallocene catalysts are disclosed in copending U.S. Application Serial Nos. 034,472; 096,075; and 095,755. In contrast to the catalysts disclosed in those applications, the catalysts useful in producing the polymers of the present invention are syndio-specific and produce a polymer with a high syndiotactic index. It was discovered that syndiotactic polypropylene has lower heats of crystallization than the corresponding isotactic polymers. In addition, for the same number of imperfections in the polymer chain, syndiotactic polymers have a higher melting point than isotactic polymers.

The metallocene catalysts of the present invention may be described by the formula $R''(CpR_n)(CpR'_m)MeQ_k$ wherein each Cp is a cyclopentadienyl or substituted cyclopentadienyl ring; R_n and R'_m are hydrocarbyl radicals having 1-20 carbon atoms, each R_n may be the same or different, and each R'_m also may be the same or different; R″ is a structural bridge between the two Cp rings imparting stereorigidity to the Cp rings, and R″ is preferably selected from the group consisting of an alkyl radical having 1-4 carbon atoms or a hydrocarbyl radical containing silicon, germanium, phosphorus, nitrogen, boron, or aluminum; Me is a group 4b, 5b, or 6b metal from the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; $0 \leqq k \leqq 3$; $0 \leqq n \leqq 4$; and $1 \leqq m \leqq 4$. In order to be syndio-specific, it was discovered that the Cp rings in the metallocene catalysts must be substituted in a substantially different manner so that there exists a steric difference between the two Cp rings, and therefore, R'_m is selected such that (CpR'_m) is a substantially different substituted ring than (CpR_n). In order to produce a syndiotactic polymer, the characteristics of the groups substituted directly on the cyclopentadienyl rings seem to be important. Thus, by "steric difference" or "sterically different" as used herein, it is intended to imply a difference between the steric characteristics of the Cp rings that controls the approach of each successive monomer unit that is added to the polymer chain to produce the syndiotactic configuration.

In a preferred catalyst useful in producing polymers of the present invention, Me is titanium, zirconium or hafnium; Q is preferably a halogen, and it is most preferably chlorine; and k is preferably 2, but it may vary with the valence of the metal atom. Exemplary hydrocarbyl radicals include methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, isoamyl, hexyl, heptyl, octyl, nonyl, decyl, cetyl, phenyl, and the like. Other hydrocarbyl radicals useful in the metallocene catalysts include other alkyl, aryl, alkenyl, alkylaryl or arylalkyl radicals. Further, R_n and R'_m may comprise hydrocarbyl radicals attached to a single carbon atom in the Cp ring as well as radicals that are bonded to two carbon atoms in the ring. Figure 1 shows the structure of a preferred catalyst isopropyl(fluorenyl) (cyclopentadienyl) hafnium dichloride. The zirconium analogue of the catalyst shown in FIGURE 1 is similarly preferred.

The catalyst may be prepared by any method known in the art. The Examples below disclose two methods of preparing the catalyst with the second method being preferred as it produces a more stable and active catalyst. It is important that the catalyst complex be "clean" as usually low molecular weight, amorphous polymer is produced by impure catalysts. Generally, the preparation of the catalyst complex consists of forming and isolating the Cp or substituted Cp ligands which are then reacted with a halogenated metal to form the complex.

The metallocene catalysts of the present invention are useful in many of the polymerization processes known in the art including many of those disclosed for the preparation of isotactic polypropylene. When the catalysts of the present invention are used in these types of processes, syndiotactic polymers are produced rather than isotactic polymers. Further examples of polymerization processes useful in the preparation of polymers described by the present invention include those disclosed in U.S. Application Serial No. 009,712 filed on February 2, 1987 and U.S. Application Serial No. 095,755 filed on September 11, 1987, the disclosures of which are hereby incorporated by reference. These preferred polymerization procedures include the step of prepolymerizing the catalyst and/or precontacting the catalyst with a cocatalyst and an olefin monomer prior to introducing the catalyst into a reaction zone.

Consistent with the prior disclosures of metallocene catalysts for the production of isotactic polymers, the catalysts of the present invention are particularly useful in combination with an aluminum cocatalyst, preferably an alumoxane, an alkyl aluminum, or a mixture thereof. In addition, a complex may be isolated between a metallocene catalyst as described herein and an excess amount of aluminum cocatalyst in accordance with the teachings of European Patent Publication No. 226,463 published on June 24, 1987 assigned to Exxon Chemical Patents Inc. with Howard Turner listed as the inventor. The alumoxanes useful in combination with the catalysts of the present invention may be represented by the general formula (R-Al-0-) in the cyclic form

and $R(R-Al-O)_n-ALR2$ in the linear form wherein R is an alkyl group with one to five carbon atoms and n is an integer from 1 to about 20. Most preferably, R is a methyl group. The alumoxanes can be prepared by various methods known in the art. Preferably, they are prepared by contacting water with a solution of trialkyl aluminum, such as, trimethyl aluminum, in a suitable solvent such as benzene. Another preferred method includes the preparation of alumoxane in the presence of a hydrated copper sulfate as described in U.S. Patent No. 4,404,344 the disclosure of which is hereby incorporated by reference. This method comprises treating a dilute solution of trimethyl aluminum in toluene with copper sulfate. The preparation of other aluminum cocatalysts useful in the present invention may be prepared by methods known to those skilled in the art.

The Examples given below illustrate the present invention and its various advantages and benefits in more detail. Two different synthesis procedures, designated as A and B, are described for both zirconium and hafnium metallocene catalysts. The general catalyst formula for the catalyst produced by these methods is iso-propyl(fluorenyl)(cyclopentadienyl) $MeCl_2$ wherein Me is either zirconium or hafnium depending on the example. Figure 1 shows the structure of the hafnium catalyst and the zirconium catalyst has essentially the same structure with Zr positioned in the place of the Hf atom.

Preparation of the Catalyst - Method A

The synthesis procedures for the catalyst were performed under an inert gas atmosphere using a Vacuum Atmospheres glovebox or Schlenk techniques. The synthesis process generally comprises the steps of 1) preparing the halogenated or alkylated metal compound, 2) preparing the ligand, 3) synthesizing the complex, and 4) purifying the complex.

In Method A, the halogenated metal compound was prepared using tetrahydrofuran ("THF") as a solvent resulting in THF bound in with the final catalyst complex. Specifically, $MeCl_4THF$ was prepared as described in Manzer, L., Inorg. Synth., 21, 135-36 (1982). In the Examples below, Me is zirconium and hafnium, but it may also include titanium or other transition metals.

The substituted dicyclopentadienyl ligand may be prepared using various processes known in the art depending upon the selection of the specific bridge or ring substituents. In the preferred embodiments shown in the Examples below, the ligand is 2,2-isopropyl(fluorene)cyclopentadiene. To prepare this ligand, 44 gms (0.25 mol) of fluorene were dissolved in 350 ml THF in a round bottom flask equipped with a side arm and dropping funnel. Contained within the funnel were 0.25 mol of methyl lithium (CH_3Li) in ether (1.4 M). The CH_3Li was added dropwise to the fluorene solution and the deep orange-red solution was stirred for several hours. After gas evolution had ceased, the solution was cooled to -78°C and 100 ml of THF containing 26.5 gms (0.25 mol) of 6,6-dimethylfulvene was added dropwise to the solution. The red solution was gradually warmed to room temperature and stirred overnight. The solution was treated with 200 ml of water and stirred for ten minutes. The organic fraction of the solution was extracted several times with 100 ml portions of diethylether, and the combined organic phases were dried over magnesium sulfate. Removal of the ether from the organic phases left a yellow solid which was dissolved in 500 ml of chloroform and recrystallized by addition of excess methanol at 2°C to yield a white powder.

The elemental analysis of the ligand showed carbon to be 91.8% by weight of the compound and hydrogen to be 7.4% by weight. This corresponds to the weight percentages for $C_{21}H_{20}$, 92.6% carbon and 7.4% hydrogen. The NMR spectrum for the ligand establishes the structure to include one cyclopentadienyl ring attached by an isopropyl bridge to a second cyclopentadienyl ring that is substituted to form a fluorenyl radical.

A syndiospecific catalyst complex was synthesized using the ligand and the metal tetrachloride-THF complex. The catalyst was formed by adding 0.05 mol of N-butyl lithium in hexane (1.6M) dropwise to a 100 ml THF solution containing 6.8 gms (0.025 mol) of the Cp ligand described above. The solution was stirred at 35°C for twelve hours after which 9.4 gms (0.025 mol) of $ZrCl_4$-2THF contained in 200 ml of THF were rapidly cannulated together with the ligand solution into a 500 ml round bottom flask with vigorous stirring. The deep orange-red solution was stirred for twelve hours under reflux. A mixture of LiCl and a red solid were isolated by removing the solvents under vacuum.

Catalyst complexes produced in accordance with Method A are noted to be somewhat impure and extremely air and moisture sensitive. As a result, in the Examples below, Method A catalysts were purified using one or more of the following purification procedures:

1. Extraction with pentane. Trace quantities of a yellow impurity contained in the solid red catalyst complex were repeatedly extracted with pentane until the pentane became colorless.
2. Fractional recrystallization. The red complex was separated from the white LiCl by dissolving it in 100 ml of toluene, filtering it through a fine porosity sintered glass frit, and forming a saturated solution by adding pentane. The red zirconium complex was isolated using crystallization at -20°C.
3. Chromotography on bio-beads. 50 gms of bio-beads SM-2 (20-50 mesh spherical, macroreticular styrene-divinylbenzene copolymer from Bio-Rad laboratories) were dried under vacuum at 70°C for 48 hours in a 30 x 1.5 centimeter column. The beads were then equilibrated with toluene for several hours. A concentrated solution of the red catalyst complex in toluene was eluted down the column with 150-200 ml of toluene. The complex was recovered by evaporating the toluene under vacuum.

Catalyst Synthesis Procedure - Method B

As an alternative synthesis procedure, Method B provides catalysts that are more air stable, more active, and produce a higher percentage of syndiotactic polypropylene. In this process, methylene chloride is used as a non-coordinating solvent. The process described below uses hafnium as the transition metal, but the procedure is adaptable for use with zirconium, titanium or other transition metals. The substituted dicyclopentadienyl ligand was synthesized in THF in the same manner as described in Method A above. The red dilithio salt of the ligand (0.025 mol) was isolated as disclosed in Method A by removing the solvents under vacuum and by washing with pentane. The isolated red dilithio salt was dissolved in 125 ml of cold methylene chloride and an equivalent amount (0 .025 mol) of $HfCl_4$ was separately slurried in 125 ml of methylene chloride at -78°C. The $HfCl_4$ slurry was rapidly cannulated into the flask containing the ligand solution. The mixture was stirred for two hours at -78°C, allowed to warm slowly to 25°C and stirred for an additional 12 hours. An insoluble white salt (LiCl) was filtered off. A moderately air sensitive, yellow powder was obtained by cooling the brown/yellow methylene chloride solution to -20°C for 12 hours and cannulating away the supernatant. The bright yellow product was washed on the sintered glass filter by repeatedly filtering off cold supernatant that had been cannulated back over it. The catalyst complex was isolated by pumping off the solvents using a vacuum, and it was stored under dry, deoxygenated argon. The process yielded 5.5 gms of catalyst complex.

The elemental analysis of the hafnium catalyst complex prepared using Method B showed that the catalyst consisted of 48.79% by weight of carbon, 3.4% hydrogen, 15.14% chlorine and 33.2% hafnium. These percentages compare with the theoretical analysis for $C_{21}H_{18}HfCl_2$ which is 48.39% carbon, 3.45% hydrogen, 13.59% chlorine and 34.11% hafnium. Similarly, zirconium catalysts produced using Method B show elemental analysis close to the expected or theoretical values. Further, some of the hafnium complexes illustrated in the Examples below were made using 96% pure $HfCl_4$ which also contains about 4% $ZrCl_4$. Still other catalyst samples were made using 99.99% pure $HfCl_4$. Differences can be seen in the molecular weight distributions of the polymers produced using the pure Hf catalyst and those produced using the catalyst which contains a small percentage of zirconium. The mixed catalyst produces a polymer with a broader molecular weight distribution than a pure catalyst system.

The Examples below illustrate the preparation of the polymers of the present invention and its various advantages in more detail. The results of the polymerization process and the analysis of the polymer are shown in Table 1 for Examples 1-17 and Table 2 for Examples 18-33.

Example 1

The polymerization of propylene was carried out using 0.16 mg of isopropyl(cyclopentadienyl)(florenyl) zirconium dichloride produced in accordance with Method A described above. The catalyst was purified using fractional recrystallization. The catalyst was precontacted for 20 minutes with a toluene solution containing 10.7% by weight of methylalumoxane (MAO) with an average molecular weight of about 1300. The alumoxane serves as a co-catalyst in the polymerization reaction. Ten cc of the MAO solution was used in the polymerization. The catalyst and co-catalyst solution was then added to a Zipperclave reactor at room temperature followed by the addition of 1.2 liters of liquid propylene. The reactor contents were then heated to the polymerization temperature, T as shown in Tables 1 and 2, of 20°C in less than about 5 minutes. During this time, prepolymerization of the catalyst occurred. The polymerization reaction was allowed to run for 60 minutes during which time the reactor was maintained at the polymerization temperature. The polymerization was terminated by rapidly venting the monomer. The reactor contents were washed with 50% methanol in dilute HCl solution and dried in vacuo. The polymerization yielded 14 gms of polypropylene "as polymerized", i.e., without any further isolations or purification.

Analysis of Polymer

The polymer was analyzed to determine the melting point Tm, the heat of crystallization Hc, the molecular weights Mp, Mw, and Mn, the percent of xylene insolubles XI, and the syndiotactic index S.I. Unless otherwise noted, the analyses were performed on the xylene insoluble fraction of the polymer which includes the syndiotactic fraction and any isotactic polymer produced. The atactic polymer was removed by dissolving the polymer product in hot xylene, cooling the solution to 0°C and precipitating out the xylene insoluble fraction. Successive recrystallizations performed in this manner result in removing essentially all atactic polymer from the xylene insoluble fraction.

The melting points, Tm, were derived using Differential Scanning Calorimetry (DSC) data as known in the art. The melting points, Tm1 and Tm2 listed in Tables 1 and 2 are not true equilibrium melting points but are DCS peak temperatures. In polypropylene, it is not unusual to get an upper and a lower peak temperature, i.e. two peaks, and both melting points are reported in Tables 1 and 2 with the lower melting point reported as Tm1 and the higher point as Tm2. True equilibrium melting points obtained over a period of several hours would most likely be several degrees higher than the DSC lower peak melting points. As is known in the art, the melting points for polypropylene are determined by the crystallinity of the xylene insoluble fraction of the polymer. This has been shown to be true by running the DSC melting points before and after removal of the xylene soluble or atactic form of the polymer. The results showed only a difference of 1-2°C in the melting points after most of the atactic polymer was removed. As shown in Table 1, the melting points were determined to be 145°C and

150°C for the polymer produced in Example 1. DSC data was also used to determine the heat of crystallization, -Hc as shown in Tables 1 and 2 measured in J/g. The melting points and -Hc were determined on the "as polymerized" sample before the atactic polymer was removed.

The molecular weights of the polymer were calculated using Gel Permeation Chromotography (GPC) analysis done on a Waters 150C instrument with a column of Jordi gel and an ultra-high molecular weight mixed bed. The solvent was trichlorobenzene and the operating temperature was 140°C. From GPC, M_p which is the peak molecular weight, M_n which is the number average molecular weight, and M_w which is the weight average molecular weight were derived for the xylene insoluble fraction of the polymer produced. The molecular weight distribution, MWD, is commonly measured as M_w divided by M_n. The values determined for this sample are shown in Table 1. GPC analysis was also used to determine the syndiotactic index, S.I.%, shown in Tables 1 and 2. The syndiotactic index is a measure of the percentage of the syndiotactic structure produced in the polymerization reaction and was determined from the molecular weight data on the samples "as polymerized."

NMR analysis was used to determine the microstructure of the polymer. A sample of the polymer produced above was dissolved in a 20% solution of 1,2, 4-trichlorobenzene/d_6-benzene and run on a Bruker AM 300 WB spectrometer using the inverse gate broad band decoupling method. The experimental conditions were: transmitter frequency 75.47 MHz; decoupler frequency 300.3 MHz; pulse repetition time 12 seconds; acquisition time 1.38 seconds; pulse angle 90° (11.5 microseconds pulse width); memory size 74K points; spectral window, 12195 Hz. Seven thousand transients were accumulated, and the probe temperature was set at 133°C. The NMR spectrum for the polymer produced and recrystallized from xylene one time is shown in Figure 2. The calculated and observed values for the spectrum are shown in Table 3 with Example 1 representing the data for the sample recrystallized once from xylene and Example 1-A representing the data for the sample recrystallized three times from xylene. The calculated values were derived using the Bernoullian probability equations as disclosed in Inoue Y., et al, Polymer, Vol. 25, page 1640 (1984) and as known in the art.

The results show that in the sample recrystallized once from xylene the percentage of racemic dyads (r) is 95%. For the sample recrystallized three times from xylene the percentage of r dyads is 98% indicating a polymer that consists of 2% or less of the meso (m) dyad. Further, the NMR spectrum shows that the meso dyads occur predominately in pairs, i.e., mm triads, as opposed to the previously known single m dyad structure in the chain. The data in Table 3 establishes that the polymer does have a novel micro-structure.

Example 2

The procedures of Example 1 were repeated except that 500 ml of toluene was used as a co-solvent in the polymerization reaction. Further, one gram of MAO was used in the polymerization, and the reaction temperature was 50°C. Fifteen grams of oil were obtained along with the polymer product. The polymer was analyzed in accordance with the procedures given above and the results are shown in Table 1.

Example 3

The procedures of Example 2 were repeated except that hafnium was used as the transition metal in the catalyst. The other reaction conditions were as shown in Table 1, and the analyzed properties of the resulting polymer are also shown in Table 1.

Examples 4 through 8

The procedures of Example 1 were repeated except for the differing reaction conditions as shown in Table 1. In addition, Example 4 used chromotography as the purification procedure and Example 5 utilized no purification procedure. The results of the polymerization and the analysis of the polymer are shown in Table 1.

FIGURES 3 and 4 show the IR spectra for the polymer produced in Examples 7 and 8 respectively. The characteristic bands at 977 and 962 cm^{-1} for syndiotactic polypropylene are readily visible. The presence of these bands reaffirm the syndiotactic structure of the polymer. The corresponding bands for isotactic polypropylene are 995 and 974 respectively.

Examples 9-16

The procedures of Example 1 were repeated except for the changes in the amounts of catalyst and co-catalyst as indicated in Table 1. Further, the catalysts in Examples 9-13 and 15 were purified using both extraction with pentane and fractional recrystallization. Example 14 used extraction with pentane and chromotography as the purification procedures. Example 16 did not use any purification procedure.

Example 17

The procedures of Example 1 were repeated except that hafnium was used as the transition metal for the catalyst. The other reaction conditions were as shown in Table 1. The catalyst was purified using extraction with pentane and fractional recrystallization. The results of the polymerization are shown in Table 1.

Examples 18 and 19

A hafnium metallocene catalyst was synthesized using Method B as described above and using the 95% pure $HfCl_4$ that contained about 4% $ZrCl_4$. The polymerization was carried out using the polymerization procedures of Example 1 under the conditions shown in Table 2. The polymers were analyzed in accordance with the procedures set forth in Example 1 and the results are shown in Table 2.

Examples 20-31

A zirconium metallocene catalyst was prepared using the synthesis procedures of Method B, and the polymerization of propylene was carried out under the conditions shown for each Example in Table 2. The polymer products were analyzed in accordance with the procedures of Example 1 and the results are given in Table 2. It should be noted that for Examples 20-22, the syndiotactic index, S.I., was determined for the xylene insoluble fraction. The syndiotactic index for these fractions were nearly 100%. The observed (obsd.) NMR spectra data for Examples 20 and 22 are shown in Table 4. The data given for Examples 20 and 22 was collected from the polymers produced in Examples 20 and 22 respectively and recrystallized once from xylene. Example 22-A is the polymer of Example 22 that is recrystallized three times from xylene.

Examples 32-33

A hafnium metallocene catalyst was prepared using the synthesis procedures of Method B. The catalyst for Example 32 was prepared using the 99% pure $HfCl_4$ while the catalyst in Example 33 was prepared from the 95% pure $HfCl_4$ that contained about 4% $ZrCl_4$. The polymerization was carried out in accordance with the procedures of Example 1 under the conditions shown for Examples 32 and 33 in Table 2. The results of the analysis of the polymer produced in these Examples are also shown in Table 2. The NMR data for Example 33 is shown in Table 4 with the sample as recrystallized once from xylene (Ex. 33) and three times from xylene (Ex. 33A).

The data shown in Tables 1-4 and in Figures 2 and 3 show that the polymers of the present invention are predominantly syndiotactic polypropylene that has high crystallinity and a novel microstructure. Particularly, the NMR data shown in Tables 3 and 4 establish that the xylene insoluble fraction consists of a very high percentage of syndiotactic polymer with very little, if any, isotactic polymer being produced. Further, the syndiotactic polymer contains a high percentage of "r" groups and "rrrr" pentads indicating that there is only a small percentage of deviations from the "...rrrr..." structure in the polymer chain. The deviations that do exist are predominantly of the "mm" type. Indeed, the results for Ex. 1-A in Table 3 show that the only deviation in the chain is of the "mm " type. The other NMR samples show the predominance of the "mm" deviation over the "m" deviation. Thus, a novel microstructure for syndiotactic polypropylene has been discovered.

The data in Tables 1 and 2 shows the high crystallinity of the polymer product. The relatively high melting points, TM1 and TM2, and the relatively high heats of crystallization, -Hc, indicate that the polymers are highly crystalline. The data further indicates a correlation between the polymerization reaction temperature, T, and the melting points, molecular weights and the heats of crystallization of the polymer. As the reaction temperature increases, all three of these properties decrease. There also seems to be a range of temperature within which the yield of polymer is maximized. This reaction temperature range will vary with the type of catalyst used but is typically 50-70° C. The concentration of methylalumoxane (MAO) also appears to affect the polymer yield. The data indicates that to a point, the greater the concentration of MAO, the higher the yield of polymer. The concentration of MAO also seems to have some effect on the amount of atactic polymer produced. MAO appears to act like a scavenger for impurities and tends to reduce the amount of atactic polymer produced.

The data further indicates a difference between the zirconium catalysts and the hafnium catalysts of the present invention. The polymers produced with the hafnium catalysts tend to be less crystalline and have lower melting points than the polymers produced with the zirconium catalysts. The data in Table 4 also shows that the hafnium catalyst produces a higher percentage of isotactic blocks in the polymer chain as reflected by the presence of the isotactic pentad mmmm.

Examples 18, 19 and 33 show the ability to achieve a broader molecular weight distribution, MWD = Mw/Mn, by use of a mixture of the catalysts described by the present invention. The catalysts in these Examples were prepared using $HfCl_4$ that contained about 4% $ZrCl_4$. The MWD of the polymer in these Examples is

significantly higher than the MWD of the polymer produced by an essentially pure hafnium catalyst - see Example 32. Thus, a mixture of two different catalysts can be used to produce a polymer with a broad MWD.

It should be further understood that the syndio-specific catalysts of the present invention are not limited to the specific structures recited in the Examples, but rather, include catalysts described by the general formula given herein in which one Cp ring is substituted in a sterically different manner. In the Examples above, the rings included an unsubstituted Cp ring and a Cp ring substituted to form a fluorenyl radical, but similar results are obtainable through the use of other ligands consisting of bridged Cp rings in which one of the Cp rings is substituted in a substantially different manner from the other Cp ring, e.g., an indenyl radical and a Cp ring, a tetramethyl substituted Cp and a mono substituted Cp ring, etc.

From the detailed description of the invention just given, it is apparent that the invention provides a novel structure of syndiotactic polypropylene. Having described but a few embodiments, it will be apparent to one skilled in the art that various modifications and adaptations may be made to the polymers as described without departing from the scope of the present invention.

TABLE 1

Method A

Example	Metal	Catalyst (mg)	MAO (cc)	T°C	Yield (g)	Tm1°C	Tm2°C	-Hc J/g	Mp/1000	Mw/Mn	S.I.%
1	Zr	10.0	10.0	20	14	145	150	43	118	2.5	62
2	Zr	10.3	1g	50	26	129	137	45	57	1.9	68
3	Hf	10.3	1g	50	12		104	17	1222		46
4	Zr	5.0	10.0	50	130	132	138	37	61		87
5	Zr	5.1	10.0	50	83	131	138	38	62		84
6	Zr	5.0	0.3g	70	22	115	127	34	71		83
7	Zr	5.1	5.0	50	68	131	140	37	60		38
8	Zr	5.1	10.0	50	110	132	140	38	60		42
9	Zr	5.1	1.0	50	14	114	126	21	58		24
10	Zr	5.0	2.5	50	34	111	122	14	60		23
11	Zr	5.1	5.0	50	68	119	130	21	60		38
12	Zr	5.0	10.0	50	78	128	137	32	64		65
13	Zr	5.0	1.0	50	83	121	132	22	59		42
14	Zr	2.6	10.0	50	85	134	140	40	62		89
15	Zr	5.1	10.0	50	110	125	134	29	60		42
16	Zr	5.1	10.0	50	115	131	138	38	62		84
17	Hf	10.3	1g	80	55	89	108		223		52

TABLE 2

Method B

Example	Metal	Catalyst (mg)	MAO (cc)	T°C	Yield (g)	Tm1°C	Tm2°C	-Hc J/g	Mw/1000	Mw/Mn	S.I.%
18	Hf	10.0	10	50	58	116	125	24	644	5.4	
19	Hf	5.0	10	50	60	117	124	24	774	4.8	
20	Zr	0.6	10	50	162	134	140	40	69	1.8	95
21	Zr	1.5	10	29	49	142	146	45	106	1.9	95
22	Zr	0.6	10	70	119		134	39	54	2.0	95
23	Zr	0.2	10	50	27	135	140	39	69	1.9	
24	Zr	0.6	10	50	162	134	140	40	69	1.8	
25	Zr	0.6	10	25	26		145	44	133	1.9	
26	Zr	0.6	10	70	119		134	39	54	2.0	
27	Zr	1.5	10	29	49	142	146	45	106	1.9	
28	Zr	2.5	10	50	141	135	141	40	70	1.9	
29	Zr	5.0	10	28	152	128	137	43	88	2.1	
30	Zr	0.5	10	60	185	128	137	37	52	1.8	
31	Zr	0.5	5	70	158	120	134	36	55	2.4	
32	Hf	2.5	10	70	96	103		19	474	2.6	
33	Hf	10.0	10	50	27	114		26	777	5.3	

TABLE 3

	Ex. 1		Ex. 1A	
	obsd.%	calc.%	obsd.%	calc.%
%r	95	95	98	98
mmmm	0.3	0.2	0	0
mmmr	0.3	0.6	0	0
rmmr	1.5	1.4	1.3	1.0
mmrr	2.4	2.9	1.9	2.1
rrmr + mmrm	1.5	1.6	0	0
mrmr	1.6	0.8	0	0
rrrr	88.0	89.1	94.7	94.7
mrrr	3.9	3.1	2.2	2.1
mrrm	0.4	0.4	0	0
dev.		0.2		0.1

TABLE 4

	EX. 20 obsd.%	EX. 22 obsd.%	EX. 22-A obsd.%	EX. 33 obsd.%	EX. 33-A obsd.%
mmmm	0	0.77	0.51	2.34	2.04
mmmr	0.23	0.45	0.31	0.73	0.76
rmmr	1.67	1.82	1.81	2.72	2.96
mmrr	3.58	4.25	4.06	5.72	6.44
mrmm + rmrr	2.27	3.23	3.57	2.87	3.12
mrmr	1.51	2.06	1.70	1.37	1.53
rrrr	82.71	77.58	78.12	75.7	74.55
mrrr	6.45	7.75	9.02	7.4	8.01
mrrm	0.68	0.73	0.93	1.08	0.55

Claims

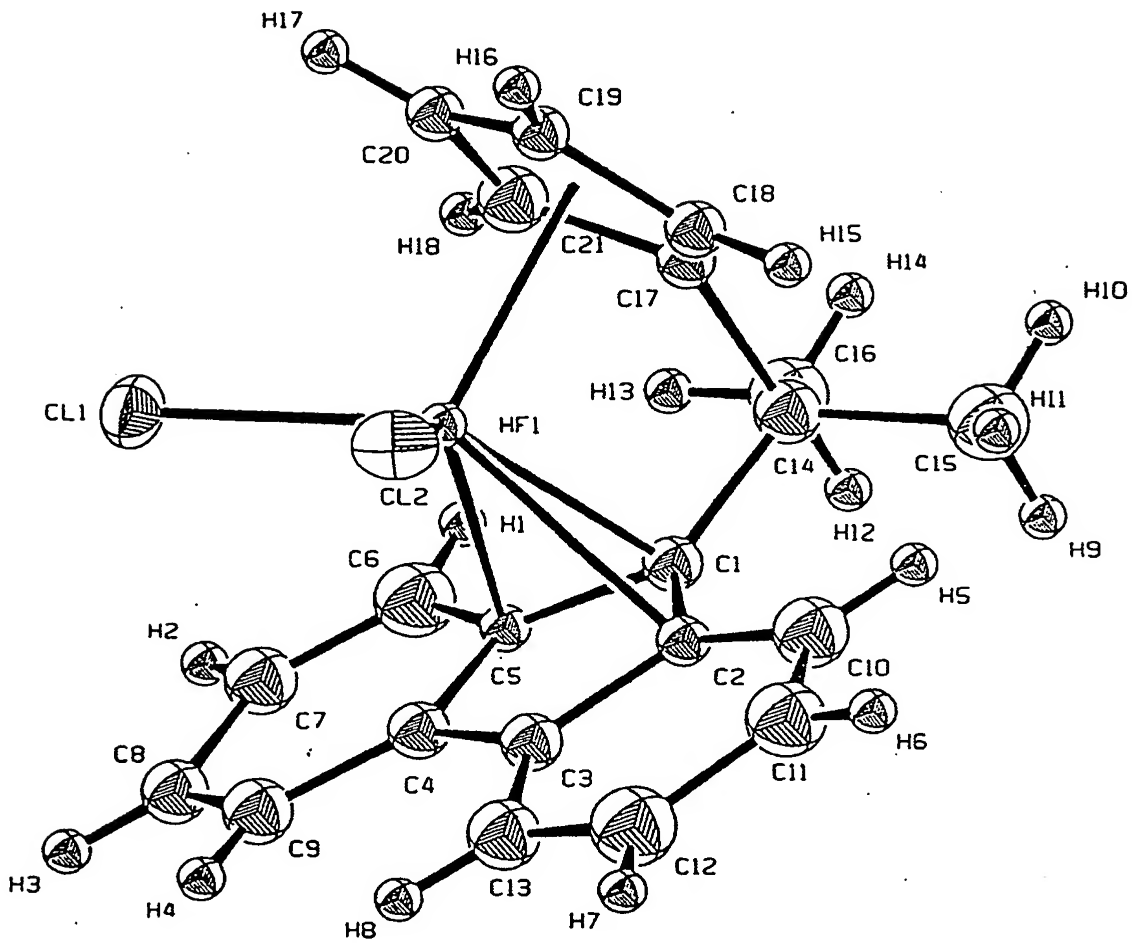
1. Syndiotactic polypropylene in which the microstructure of the polymer chain consists of blocks of repeating racemic (r) dyads being connected predominantly by units consisting of a meso triad (mm).

2. The syndiotactic polypropylene of Claim 1 wherein greater than 40% of the connecting units are a meso triad (mm).

3. The syndiotactic polypropylene of Claim 1 wherein the polymer structure consists of greater than 80% racemic (r) dyads.

4. The syndiotactic polypropylene of Claim 1 wherein the polymer structure consists of greater than 95% racemic (r) dyads.

5. The syndiotactic polypropylene of Claim 1 wherein the molecular weight distribution (Mw/Mn) is greater than 3.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C14
C15
CL2
H12
H1
C1
H9
C6
H5
H2
C5
C2
C10
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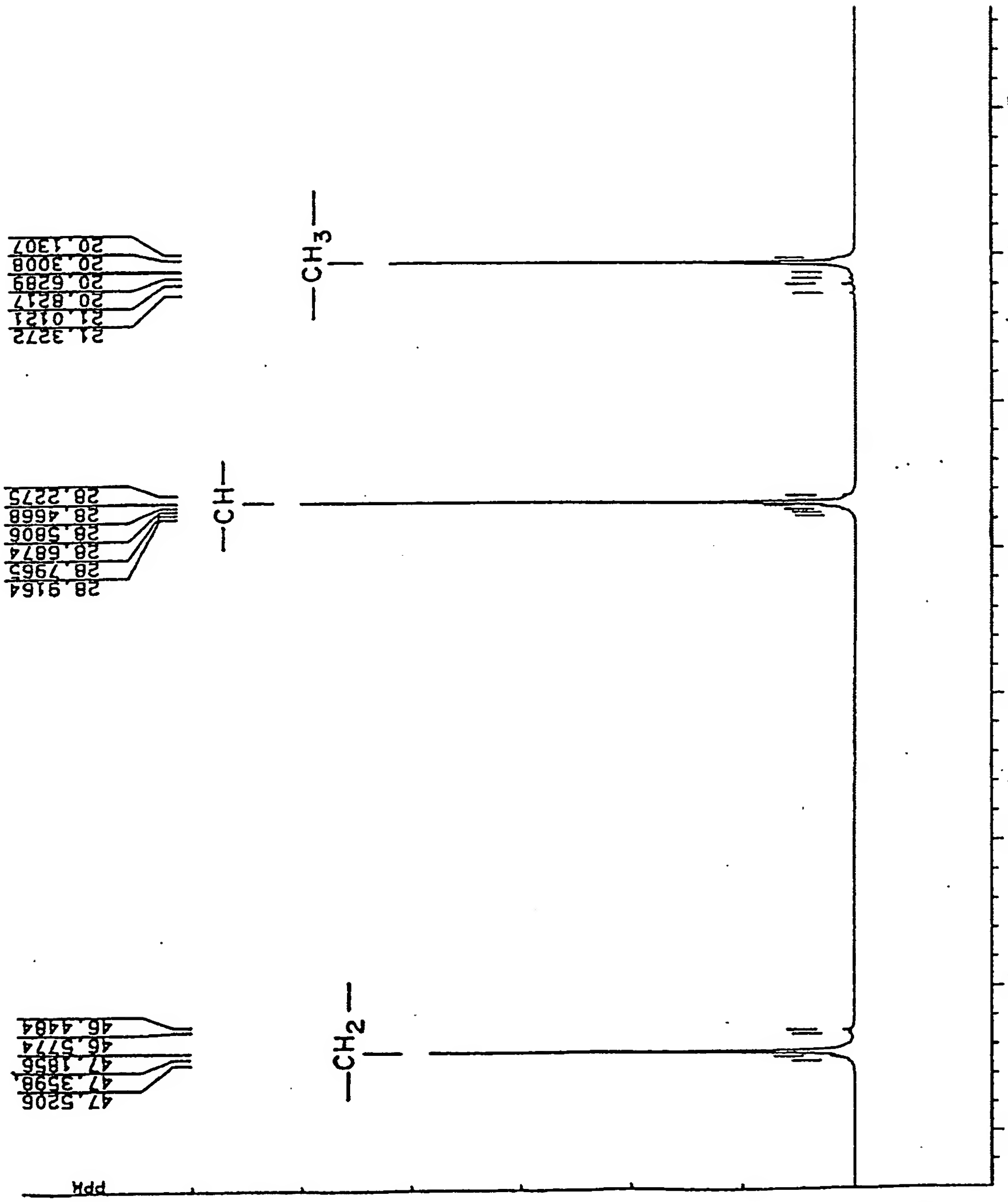
H8
H7

FIG.1



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PPM

FIG.2

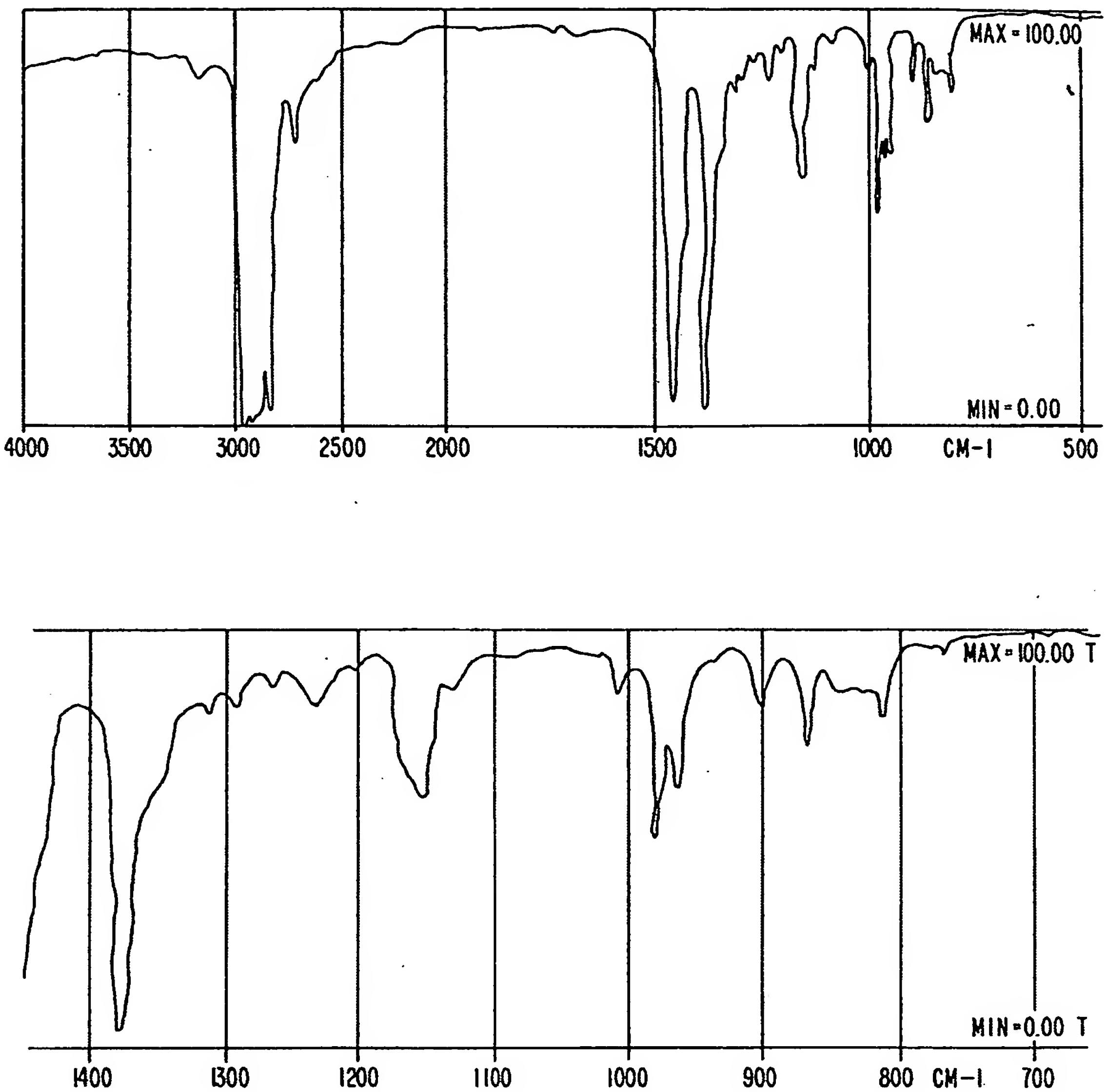

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FIG. 3

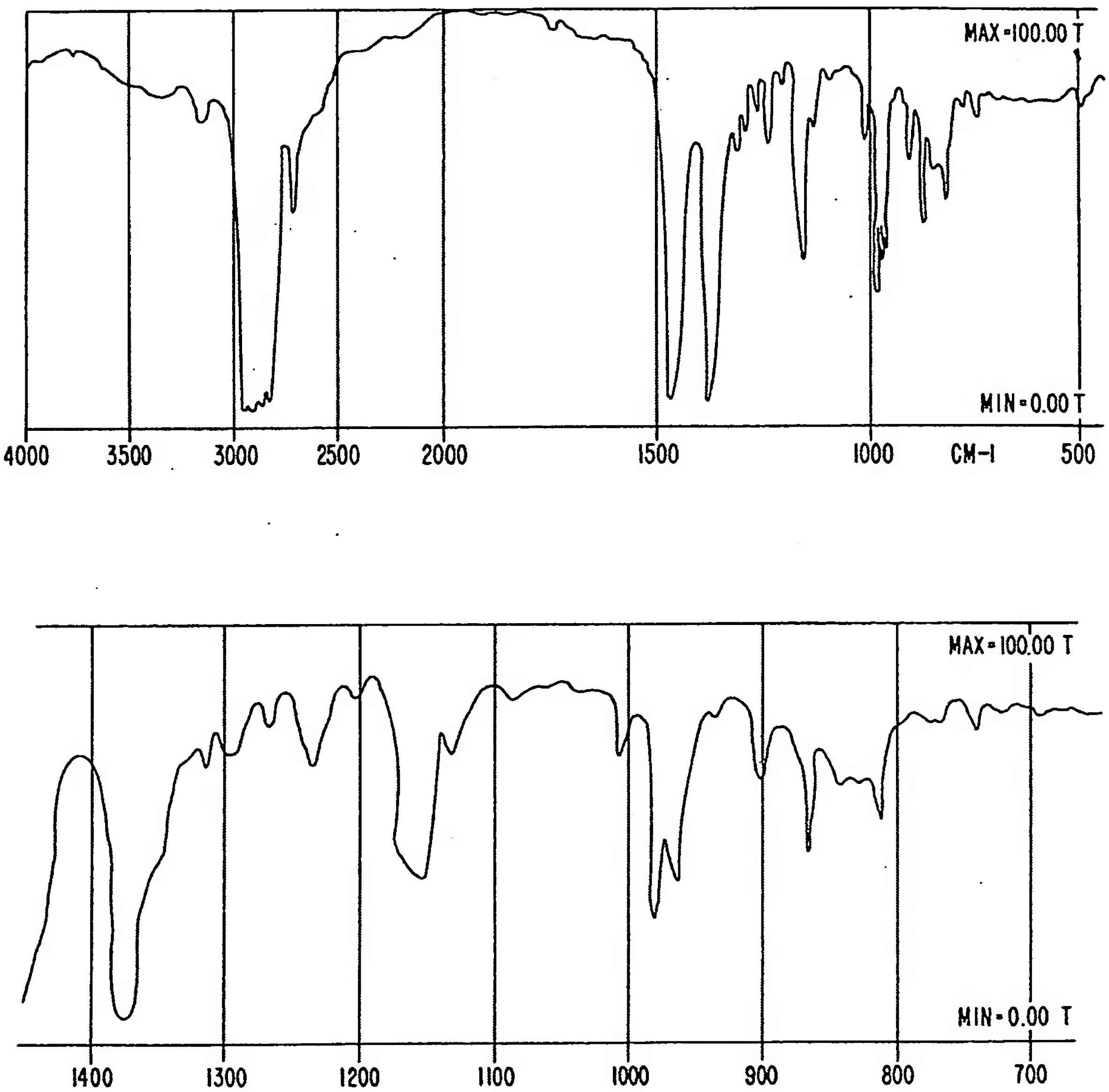
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FIG. 4